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(54) PROCESS FOR PREPARING TITANIUM TRICHLORIDE CATALYST COMPONENT

(71) We, STAUFFER CHEMICAL COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of Westport, Connecticut 06880, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for preparing a titanium trichloride catalyst component.

In the past, a number of prior art patents have suggested ball milling or grinding titanium trichloride materials in order to form a polymerization catalyst. In a number of patents, either no temperature range for this operation is given or ball milling at room temperature is suggested. Examples of prior art patents which suggest the use of such an operation are U.S. Patent Nos. 3,032,510; 3,046,266; 3,130,003; and 3,814,743.

In addition to the foregoing references, which are of merely general interest to the present invention, certain prior art patents have appeared which contain suggestions for ball milling titanium trichloride materials at temperatures greater than room temperature. In U.S. Patent No. 3,639,375 it is suggested that a temperature range from 20 to 70°C. be used when a titanium trichloride complex that has been modified with at least one electron donor molecule is ground. Another reference which contains a similar teaching is Belgian Patent No. 807,714 which discloses a grinding temperature of from 0 to 50°C. when a titanium trichloride complex and a nitrogen or phosphorus atom-containing modifier are ground. One additional reference is U.S. Patent No. 3,701,763 which teaches grinding at from −20 to +100°C. The present invention differs from these prior art processes since, according to the present invention, the grinding is carried out in the absence of any modifier for the said titanium trichloride material. A more pertinent reference to the present invention is, however, U.S. Patent No. 3,461,083, which utilizes a grinding temperature of from 100 to 125°C. and a certain class of metallorganic compounds in the ball milling of titanium trichloride materials and which specifically states that grinding of titanium trichloride alone at temperatures higher than 40°C. results in a lowering of the catalytic activity of the final catalyst. Furthermore, U.S. Patent No. 3,688,992 teaches that it is essential to ball mill the $TiCl_3$ material below 80°C., for example, at from 20 to 60°C., but states nothing about activity changes if the grinding temperature is from 45 to 70°C. as compared to ball milling at room temperature.

It has also unexpectedly been found that a titanium trichloride complex that is formed by reducing titanium tetrachloride using metallic aluminium may be ground at a temperature of from 45 to 70°C. to yield a catalyst component which, when combined with conventionally used organo-aluminium compounds, gives an activity which is superior to that shown when the grinding is carried out at room temperature. It is also possible to activate a catalyst component more quickly by using the present invention than is possible if the catalyst component is ground at room temperature.

The titanium trichloride material which is to be ground in the process according to the present invention is well known to persons skilled in the art of olefin polymerization. It is obtained by reduction of $TiCl_4$ using metallic aluminium and is a complex compound of titanium (III) chloride and aluminium having the formula: $3TiCl_3.AlCl_3$. A suitable material of this type is "$TiCl_3A$" from Stauffer Chemical Compony, Specialty Chemical Division, Westport, Connecticut, U.S.A.

The grinding of the above-identified titanium (III) trichloride complex is carried out in conventional milling apparatus in the absence of modifiers in an inert atmosphere, such as nitrogen or argon, which is free of oxygen, at a temperature of from 45 to 70°C., preferably from 50 to 60°C., for a period of time which is effective in reducing the catalyst

component to the pulverulent state and in enhancing the activity of the said catalyst. Milling apparatus, such as ball mills, vibratory mills and impact mills, may be used. One suitable apparatus afor use in the present process is disclosed in U.S. Patent No. 3,688,992. External heat may be provided if needed to the apparatus that is used, for example, by infra-red radiation. The activity of the catalyst containing the product according to the present invention will generally be from 1300 to 1750 g. of polymer product per gram of catalyst, most generally from 1400 to 1600 g. of polymer product per gram of catalyst.

The period of grinding that is needed will be largely dependent upon the type of ball mill apparatus which is used. Laboratory ball mills and certain plant production mills will require grinding for periods ranging from 24 to 90 hours, although the particular type of apparatus shown in U.S. Patent No. 3,688,992 will merely require a grinding period of from 5 to 24 hours, preferably from 7 to 10 hours. Apparatus which subjects the material to more intense grinding will require shorter grinding times than that which has a less intense grinding action.

When measuring the temperature, it is important that the actual temperature in the interior of the mill be either measured directly or extrapolated from prior runs. In most mills, the exterior temperature of the apparatus is somewhat lower than the actual temperature generated by frictional effects of the milling operation. For example, it has been found that milling at " room temperature " causes an actual temperature of about 35°C. in the interior of the mill. This temperature gradient may be influenced, for example, when a ball mill is used, by parameters, such as the configuration of the mill, the speed of rotation of the ball mill and the weight ratio of material to be ground to the balls contained in the ball mill. For example, a higher speed of rotation will generally result in an increase of temperature inside the mill. Temperatures in excess of about 70°C. should be avoided since agglomeration of the catalyst component and subsequent inactivity of the final catalyst may result.

The product produced by the process according to the present invention, is combined with conventional organoaluminium compounds using known techniques for use in the polymerization of alpha olefins using conventional reaction conditions for such a polymerization.

Suitable organoaluminium compounds are those conventionally used, particularly alkyl compounds of aluminium of which the following are examples: trimethyl aluminium, triethyl aluminium, tributyl aluminium, triisobutyl aluminium, methyl aluminium sesquichloride, ethyl aluminium, sesquichloride, diethyl aluminium chloride, ethyl aluminium dichloride, dibutyl aluminium chloride and diethyl aluminium sesquibromide. Ethyl aluminium compounds, such as triethyl aluminium, ethyl aluminium sesquichloride and diethyl aluminium chloride, are preferred as the organoaluminium compounds.

The thus-produced catalyst is suitable for use in the production of polymers of alpha-olefins having from 2 to 8 carbon atoms, including propylene homopolymers, copolymers of propylene and ethylene, ethylene homopolymers, and polymers of butene-1, 3-methylbutene-1, and 4-methylpentene-1. The polymerization of such monomers is generally carried out at temperatures of from 10 to 150°C. using pressures of from 0.5 to 100 atmospheres.

In general, from 0.001 to 0.02 millimole of the complex compound is used per mole of alpha olefin monomer. The molar ratio of complex compound to organo-aluminium compound is from 1:0.5 to 1:20.

The following Examples illustrate the present invention.

EXAMPLE 1

This Example illustrates the general preparation of a pulverulent, aluminium-reduced, titanium trichloride catalyst component.

50 grams of titanium trichloride obtained by reducing titanium tetrachloride using aluminium was charged into an 11 cm. inner diameter, 15 cm. long stainless steel mill in a tightly controlled dry box under nitrogen. The titanium trichloride was a co-crystallized product corresponding to the formula:

$$3TiCl_3 . AlCl_3 \text{ (" } TiCl_3A \text{ ")}$$

To the mill was then charged 875 grams of 1 cm. diameter magnetized stainless steel balls and the mill was subsequently closed so as to be air-tight. It was rotated at 110 rpm for a variety of times and temperatures as described in Example 3 below. The temperature was maintained via a system comprising a thermocouple inserted in an oil well inside the mill, a temperature controller and a temperature recorder. External heat was provided via infra-red radiation. At the end of the grinding, the catalyst component was transferred to a jar in the dry box and was tested, as outlined in Example 2, for activity and isotactic index.

EXAMPLE 2

This Example sets forth the testing procedure that was utilized to determine the activity and isotactic index of the polymer product formed by using the type of catalyst components described in Example 1.

To a one gallon jacketed autoclave equipped with a stirrer that was set at 600 rpm. was charged 1 litre of dry heptane. About 0.3 grams of a $TiCl_3$ catalyst preparation formed in

accordance with Example 1 was suspended in the heptane under a nitrogen atmosphere and 8 ml. of a 20%, by weight, solution of diethyl aluminium chloride in heptane was added. An additional 1 litre of dry heptane was charged into the autoclave and the autoclave was then closed. The temperature was raised to 70°C., the autoclave was vented, hydrogen gas (3.2 lbs/in^2) was added and propylene which had been purified by being passed through a molecular sieve resin (size 4A) and through a column of a copper-based catalyst to remove trace amounts of oxygen, was added. The polymerization took place within four hours. At the end of this period, the catalyst was inactivated by addition of a propanol/water mixture and the polymer product was filtered, dried at 70°C. overnight and was weighed. About 10 grams of the dry polymer was extracted with heptane for three hours in a Soxhlet apparatus. The percent amount of the non-extracted portion of the polymer was designated "C_{7i}". From an aliquot of the filtrate was determined, via solvent evaporation, the amount of the soluble or atactic polymer that was produced.

The activity was defined as the amount of dry solid, polymer (obtained from the reaction) in grams per gram of $TiCl_3$-containing catalyst preparation.

The isotactic index (II) was defined by the following formula:

$$II = \frac{C_{7i} \times \text{Solid Polymer}}{\text{Total Polymer Produced}}$$

The total polymer produced includes the above-described insoluble (isotactic) and soluble (atactic) polymer portions.

EXAMPLE 3

The Table set forth below gives the activity and isotactic index values for a variety of catalyst components formed by the procedure of Example 1 and tested as described in Example 2. A variety of temperatures and times were used for the grinding operation.

Temp. (°C)	Time of Grinding(hrs)	Activity	Isotactic Index
Room temp.*	24	460	85.2
Room temp.	48	619	82.6
Room temp.	72	1070	88.2
Room temp.	96	1070	88.2
50°C.	24	750— 830	84.5—85.0
50°C.	48	1400—1550	86 —89
50°C.	72	1400—1550	86 —89
50°C.	96	1260—1340	88.6—89.3

*the "actual" temperature inside the ball mill was about 35°C. Ball milling at from 75 to 100°C. for about 40 hours or more will give inferior activity, i.e. an activity of from 850 to 950.

The above data indicate the increased activity of catalysts containing the titanium trichloride catalyst component obtained according to the present invention.

WHAT WE CLAIM IS:—

1. A process for the preparation of a catalyst component which, when combined with an organoaluminium compound, may be used in the polymerization of one or more alpha olefins, which comprises grinding titanium trichloride, obtained by reducing titanium tetrachloride using metallic aluminium, in the absence of a modifier for the said titanium trichloride and in the absence of oxygen at a temperature of from 45 to 70°C for a period of time sufficient to prepare a pulverulent catalyst component of enhanced activity.

2. A process as claimed in claim 1 in which the said temperature is from 50 to 60°C.

3. A process as claimed in claim 1 or claim 2 in which the said period is from 5 to 90 hours.

4. A process as claimed in claim 3 in which the said period is from 5 to 24 hours.

5. A process as claimed in claim 1 substantially as herein described.

6. A process as claimed in claim 1 substantially as herein described with reference to any one of the Examples.

7. A catalyst component when prepared by a process as claimed in any of claims 1 to 6.

8. A catalyst for the polymerization of one or more alpha olefins which comprises an organoaluminium compound and a component as claimed in claim 7.

9. A catalyst as claimed in claim 8, the activity of which is from 1300 to 1750 grams of polymer product per gram.

10. A process for the polymerization of one or more alpha olefins which comprises polymerizing the alpha olefin(s) in the presence of a catalyst as claimed in claim 8 or claim 9.

11. A process as claimed in claim 10 substantially as herein described.

12. A process as claimed in claim 10 substantially as herein described with reference to any one of the Examples.

13. An alpha olefin polymer when prepared by a process as claimed in any of claims 10 to 12.

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